

III.A.5 Functionally Graded Cathodes for Solid Oxide Fuel Cells

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Objectives

- Elucidate the oxygen reduction mechanism that occurs at the cathode of a solid oxide fuel cell (SOFC) using electrochemical performance measurements and *in-situ* spectroscopic techniques.
- Identify the rate-limiting step of the oxygen reduction mechanism under desired operating conditions.
- Develop a model to predict cathode performance considering cathode material, microstructure, and operating conditions.
- Use results from experiments and model calculations for more rational design of cathode microstructure and material.
- Optimize the performance of a mixed ionic/electronic conductor (MIEC) cathode.

Approach

- Prepare fuel cell samples with well-defined cathode surfaces using standard micro-fabrication techniques to quantify and vary the relative amounts of different reaction areas.
- Examine, *in-situ*, the presence of adsorbed oxygen species and the change in the surface structure of candidate fuel cell cathode materials under various operating conditions using Fourier transform infrared emission spectroscopy (FTIRES) and Raman microspectroscopy.
- Fabricate cathodes graded in both composition and microstructure using a combustion chemical vapor deposition (CCVD) process.
- Test the performance of all generated samples using electrochemical impedance spectroscopy (EIS).
- Develop mathematical models to simulate various possible oxygen reduction reaction schemes.
- Use computer modeling to calculate the potential and current distributions throughout the SOFC electrolyte and cathode under different operating conditions and geometrical configurations.

Accomplishments

- Patterned platinum electrodes were fabricated with feature sizes varying from 2-100 μm on yttria-stabilized zirconia (YSZ) substrates. The patterned electrodes were tested using EIS.
- Patterned lanthanum strontium manganese oxide (LSM) electrodes were fabricated with a 2 μm feature size on YSZ substrates. The patterned electrodes were tested using EIS.
- Infrared emission spectra were recorded using FTIRES for $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC), $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ (LSF), $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSC), and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) cathode materials as a function of temperature, oxygen partial pressure, and applied potential. Peaks attributed to adsorbed superoxide (O_2^-) and peroxide (O_2^{2-}) ions were observed in the spectra, indicating that during oxygen reduction on these cathodes, the oxygen molecule reduces before dissociating into oxygen atoms.

- An atomic force microscope (AFM) tip was used to enhance the Raman scattering signal of our Raman micro-spectrometer. This tip-enhanced Raman scattering (TERS) effect has increased the sensitivity of the Raman system to analyze the surface of our candidate cathode materials.
- Successfully created electrodes with compositional and structural gradients by changing precursor composition and needle size in our CCVD system. The cathode consisted of three porous layer structures, with about 5 μm thick 60 wt.% LSM–40 wt.% gadolinia-doped ceria (GDC) fine agglomerates (0.5 μm diameter) at the bottom (close to YSZ electrolyte), followed by 5 μm thick 30 wt.% LSM–30 wt.% LSC–40 wt.% GDC fine agglomerates (0.5 μm diameter), and topped with 15 μm thick 60 wt.% LSC–40 wt.% GDC coarse agglomerates (2–3 μm diameter) on the air side.
- The current and potential distributions through the SOFC electrolyte have been analyzed under different geometrical configurations.
- Several oxygen reduction reaction mechanisms have been proposed and are currently in the evaluation phase.

Future Directions

- Generate and test different micro-patterned electrode configurations to quantify the relative reactivity of different possible reaction sites.
- Further analyze the FTIRES spectra to obtain reaction kinetics parameters to be used in our mathematical models.
- Use Raman and infrared spectroscopy to identify the specific catalytic site where the oxygen molecule is reduced and dissociates.
- Introduce microstructural and compositional variations into the computer modeling.
- Quantitatively analyze porosity of each layer of the functionally graded cathodes produced by CCVD and correlate microstructure with processing conditions.

Introduction

As the operating temperature of a solid oxide fuel cell (SOFC) is lowered to reduce the system costs, the cathode/electrolyte interface begins to limit the cell performance. Various processes are associated with this interface: the transport of oxygen gas through the porous cathode, the adsorption of oxygen onto the cathode surface, the reduction and dissociation of the oxygen molecule (O_2) into the oxygen ion (O^{2-}), and the incorporation of the oxygen ion into the electrolyte for it to be transported across to the anode. A strictly electronic conductor cathode permits the reduction of oxygen to occur only at the triple phase boundary (TPB) between the oxygen gas, the cathode, and the electrolyte. By using a mixed ionic/electronic conductor (MIEC) as a cathode material, the electrochemically active area extends from just the TPB to the entire cathode surface.

This project comprises four research areas:
(1) the fabrication and testing of micro-patterned

cathodes to compare the relative activity of the TPB to the rest of the cathode surface, (2) the use of Fourier transform infrared emission spectroscopy (FTIRES) and Raman spectroscopy to analyze the oxygen reduction mechanism on the cathode surface, (3) the use of mathematical modeling to predict cathode performance based on different geometries and microstructures, and (4) the fabrication of cathodes that are graded in composition and microstructure to generate large amounts of active surface area near the cathode/electrolyte interface while creating a network of larger pores further from the interface to accommodate gas flow.

Approach

Micro-patterned electrodes were fabricated on YSZ substrates using standard photolithographic processes. Each test sample features an array of identical electrodes covering a surface area of 36 mm^2 . The procedure was first demonstrated using platinum electrodes, after which LSM electrodes were fabricated. The LSM patterned electrodes were

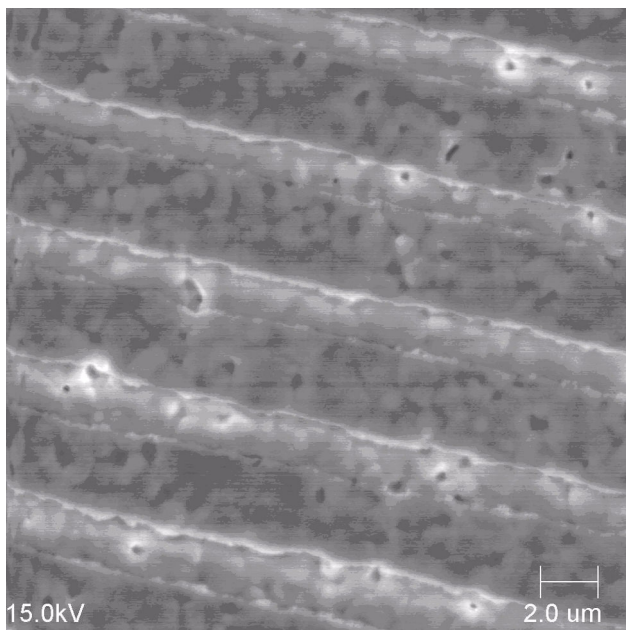


Figure 1. LSM lines on the YSZ electrolyte showing good TPB resolution. LSM electrode width is 2 μm with an electrode thickness of 0.25 μm .

characterized using electrochemical impedance spectroscopy (EIS). Characteristic impedance loops were generated from which the cathode/electrolyte interfacial resistance was calculated as a function of temperature and TPB length.

For the spectroscopic studies, porous films of candidate cathode materials (LSM, LSF, LSC, SSC) were painted on YSZ substrates and placed in a chamber designed for *in-situ* FTIRES experiments. Emission spectra from the cathode surface were recorded as a function of applied potential, partial pressure, and temperature. For kinetics information, emission spectra were taken continuously as the atmosphere inside the chamber was switched from argon to a desired oxygen partial pressure and then back again to argon. Further, Raman microspectroscopy was used to confirm the peak assignments made from the FTIR emission spectra and to analyze the surface structure of the cathode.

The current and potential distributions through the cathode and electrolyte were calculated using finite element analysis in Femlab software. The initial model was composed of a dense electrolyte covered by an air channel and dense electrode, a representative model for cells with patterned

electrodes. The steady-state distributions were calculated initially with the TPB being the only active region for electrochemical reactions (the case when a pure electronic conductor such as Pt is used as the electrode). The activity of regions other than the TPB (e.g., when a mixed conductor is used as an electrode) and porosity in the cathode will be added after optimization of the present geometry.

Combustion chemical vapor deposition (CCVD) was used to fabricate SOFC cathode films of variable composition and microstructure. In this process, a fuel containing a precursor to the desired oxide composition is sprayed through a flame at the end of a needle and deposited onto a substrate. Two approaches were attempted to control the composition and porosity of the deposited layer: (1) varying the needle-tubing size and the concentration of a precursor/fuel solution, and (2) using a solid oxide powder/fuel suspension rather than a solution. The deposited oxide films were mixtures of LSM (an electronic conductor), GDC (an ionic conductor), and LSC (a mixed ionic/electronic conductor). Three layers of varying composition and porosity were deposited on each YSZ substrate. The performance of each functionally graded cathode was characterized using EIS.

Results

We have succeeded in depositing both platinum and LSM patterned electrodes on YSZ substrates of varying feature size. By reducing the feature size, the amount of TPB can be increased rapidly while maintaining the same amount of surface area. Figure 1 shows a scanning electron micrograph of patterned electrode lines 2 μm in width. This resolution is critical to accurately quantify the dependence of cathode performance on TPB length. The cathode/electrolyte interfacial resistance was calculated from the characteristic impedance loops shown in Figure 2(a). Figure 2(b) shows the interfacial conductance (the inverse of the resistance) plotted as a function of the TPB length. This figure demonstrates the expected trend that as the relative amount of electrochemically active area (the TPB) increases with respect to total surface area, the conductivity of the electrode also increases. An expected plateau of LSM impedance at large TPB lengths was not accurately resolved, indicating that for a

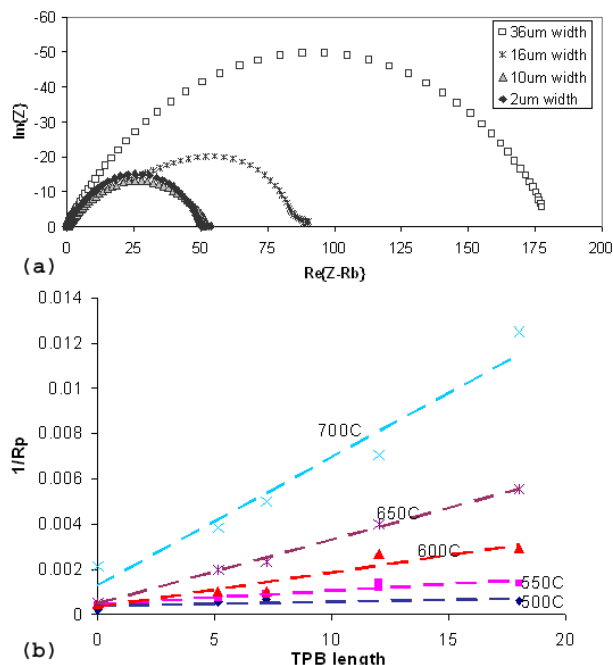


Figure 2. (a) Typical impedance loops of patterned LSM electrodes at 700°C. (b) Plot of interfacial conductance versus TPB length.

predominately electronic conductor such as LSM, the active region of the TPB extends less than 1 μm from the TPB itself. One micron is half of the current minimum possible feature size. Process parameters are being developed to fabricate LSM electrodes with sharply reduced feature sizes through the use of electron-beam lithography.

Figure 3 shows a typical series of emission spectra of an SSC cathode as the atmosphere switches from argon to 1% oxygen. As the sample is exposed to an oxygen-containing environment, the baseline shifts from horizontal to curved, and a series of peaks emerge from the baseline. For purposes of clarity, the spectra obtained as the atmosphere was switched from 1% oxygen back to argon have been omitted; however, the baseline does indeed reverse from curved back to horizontal, and the peaks in the 800 to 1250 cm^{-1} region slowly disappear. The baseline shift has been attributed to changes in the properties of the bulk electrode material and will be analyzed at a later time. The spectral features from 1400 to 1800 cm^{-1} and from 2300 to 2500 cm^{-1} are common to water vapor and carbon dioxide and thus result from random fluctuations in the carbon dioxide

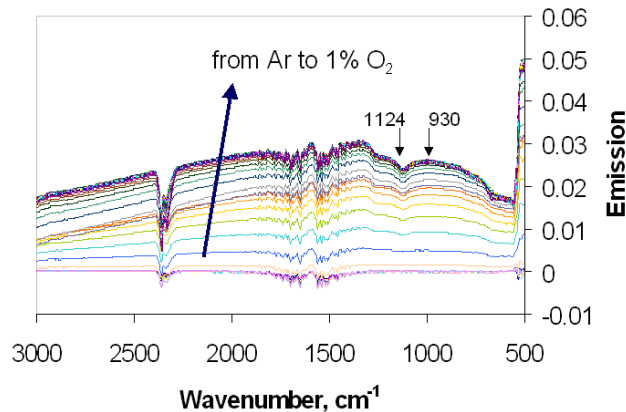


Figure 3. FTIR emission spectra for SSC pellet at 700°C as sample atmosphere changes from argon to 1% oxygen. All spectra are compared to a background spectrum measured in argon.

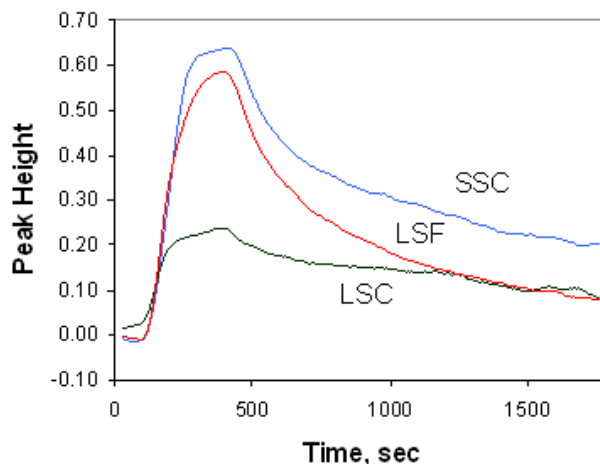


Figure 4. Plot of the height of 1124 cm^{-1} peak during gas switching experiment from argon to 1% O₂ and back to argon for different cathode materials at 600°C.

and water vapor concentrations between the emission sample chamber and the FTIR detector. The only peaks that related directly to the change in atmosphere were those located between 800 and 1250 cm^{-1} . The peaks at approximately 1236 and 1124 cm^{-1} were assigned to adsorbed superoxide (O_2^{1-}) species, while the features around 930 cm^{-1} were attributed to adsorbed peroxide (O_2^{2-}) species. The presence of the reduced oxygen molecular species on the surface demonstrates that for oxygen reduction on this cathode material, the adsorbed O_2 molecule is reduced before it dissociates. Further,

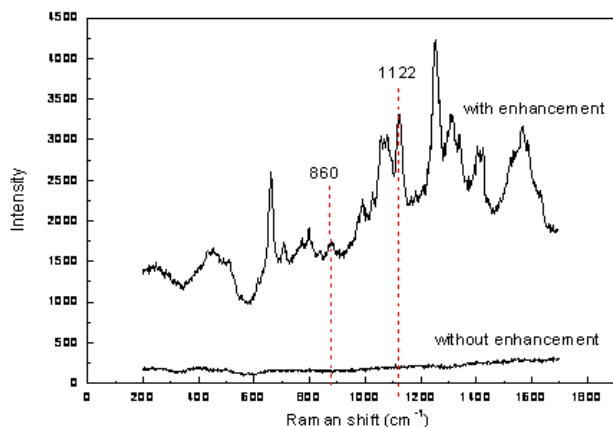


Figure 5. Raman spectra of thin film LSM with and without the tip enhancement.

since the reduced oxygen species are observable on the surface, the rate-limiting step for this mechanism is not the initial reduction of O_2 . Further studies are necessary to discern which step after the initial reduction is the exact rate-limiting step.

To quantify the concentration of adsorbed oxygen species on the surface, the height of the 1124 cm^{-1} superoxide peak was calculated by subtracting away the curved baseline. Figure 4 shows the change in the 1124 cm^{-1} peak intensity as the atmosphere was switched from pure argon to 1% O_2 for five minutes and then back to argon for SSC, LSF, and LSC at 600°C . SSC had the greatest intensity, indicating the largest concentration of surface species and thus the greatest amount of oxygen reduction activity of the three materials. This result is consistent with electrochemical performance data of the three materials under similar operating conditions. This time-dependent data is being further analyzed to obtain kinetic parameters of the oxygen reduction mechanism, which can be used for our mathematical modeling of the system.

Shown in Figure 5 are the Raman spectra of a thin LSM film with and without the presence of an atomic force microscope (AFM) tip near the film surface. It can be seen that the presence of the AFM tip dramatically enhanced the intensity of the Raman scattering signal; many new peaks appeared in the spectrum. The two peaks at 860 and 1122 cm^{-1} are considered to be surface-adsorbed peroxide and superoxide species. Further investigations into these

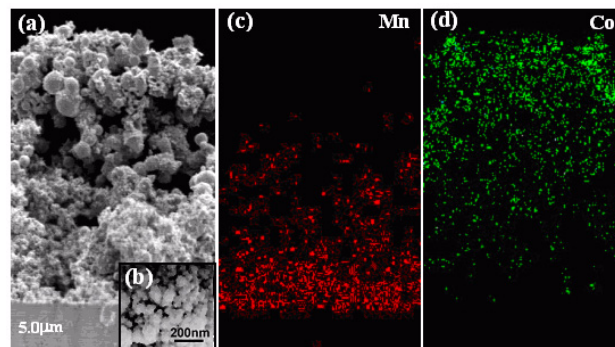


Figure 6. (a) Cross-sectional fracture surface of the functionally graded cathode fabricated on an YSZ pellet using a combustion CVD process, (b) Higher magnification image of the cathode showing the nanostructure, (c) EDS dot mapping showing manganese distribution on the cross-section surface, and (d) EDS dot mapping of cobalt distribution.

tip-enhanced Raman scattering (TERS) spectra should yield valuable information about the exact structure of the cathode surface.

Shown in Figure 6(a) is a cross-sectional view (as fractured) of a half-cell with composite cathode supported by a $240\text{ }\mu\text{m}$ thick dense YSZ electrolyte. The cathode, fabricated by CCVD, consists of three porous layer structures and is graded in both microstructure and composition, with about $5\text{ }\mu\text{m}$ thick 60 wt.% LSM–40 wt.% GDC fine agglomerates ($0.5\text{ }\mu\text{m}$ diameter) at the bottom (close to YSZ electrolyte), followed by $5\text{ }\mu\text{m}$ thick 30 wt.% LSM–30 wt.% LSC–40 wt.% GDC fine agglomerates ($0.5\text{ }\mu\text{m}$ diameter), and $15\text{ }\mu\text{m}$ thick 60 wt.% LSC–40 wt.% GDC coarse agglomerates ($2\text{--}3\text{ }\mu\text{m}$ diameter) on the top (air side). The two bottom layers are actually nanostructured, as shown in the inset Figure 6(b), offering extremely high surface area for oxygen reduction. Energy dispersive spectroscopy (EDS) dot mapping revealed the compositional changes on the cross-sectional micrograph. As shown in Figure 6(c), manganese content gradually declined from YSZ/LSM–GDC interface to LSC–GDC airside, while the cobalt signal exhibited the opposite trend as shown in Figure 6(d). The manganese-rich layers provide fast electrochemical reaction rates, high chemical stability, and a satisfying match in thermal expansion coefficient with YSZ electrolyte. Meanwhile, the

large interconnected pore channels within the coarse top layer facilitate oxygen gas mass transport through the cathode. The cobalt-rich top layer has high conductivity for efficient current collection.

Conclusions

Standard electrochemical testing of normal SOFC samples compares the overall performance of candidate cathode materials without directly revealing the reasons for the differences in performance between materials. By incorporating micro-patterned electrodes into our standard SOFC electrochemical testing and supplementing this testing with *in-situ* spectroscopic techniques, we have created a system to identify where, how, and to what extent the cathode reactions occur for different materials under different operating conditions. By deducing the rate-limiting step of the oxygen reduction mechanism, we can more specifically design more catalytically active cathode materials. Then, by quantifying the relative electrochemical reactivity of the different active regions of the cathode, we can use mathematical modeling to optimize the microstructure of the cathode. Finally, further refinement of the CCVD process will also allow us to create these optimized microstructures from the desired materials.

Publications

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8. E. Koep, C. Compson, Z. Zhou and M. Liu, "A Photolithographic Process for Investigation of Electrode Reaction Sites in Solid Oxide Fuel Cells", *Solid State Ionics*, Under review May, 2004.
9. Y. Liu, S. Zha, and M. Liu, "Nano-composite Electrodes Fabricated by a Particle-Solution Spraying Process for Low-Temperature SOFCs", *Chem. Mater.*, accepted.

Patents

1. Y. Liu and M. Liu, "A Combustion Spray Process for Fabrication of Films and Coatings", US Provisional Patent Application, filed.